General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

DOE/NASA/0067-79/1
NASA CR-159572

TECHNOLOGY DEVELOPMENT FOR PHOSPHORIC ACID
FUEL CELL POWERPLANT (PHASE II)

LARRY CHRISTNER
ENERGY RESEARCH CORPORATION

MARCH, 1979

PREPARED FOR
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LEWIS RESEARCH CENTER
UNDER CONTRACT DEN 3-67

FOR
U.S. DEPARTMENT OF ENERGY
ENERGY TECHNOLOGY
DIVISION OF FOSSIL FUEL UTILIZATION

TECHNOLOGY DEVELOPMENT FOR PHOSPHORIC ACID FUEL CELL POWERPLANT (PHASE II)

LARRY CHRISTNER
ENERGY RESEARCH CORPORATION
3 GREAT PASTURE ROAD
DANBURY, CONNECTICUT 06810

MARCH, 1979

ENERGY RESEARCH CORPORATION

EXECUTIVE SUMMARY

Component Development

- Bipolar plates for 12 in. x 17 in. (1200 cm^2) cells
  are regularly molded with approximately 80% acceptance
  rate.

- Blistering during post-cure heating of bipolar plates
  was eliminated by decreasing the heating rate.

- Bipolar plates with lower resin content (25 wt% in-
  stead of 33 wt%) have been successfully molded.

- Scale-up of the bar-cast SiC matrix for 1200 cm^2 cells
  is completed. Large batch mixing using a ball mill
  technique looks promising.

- An acid inventory control member (AICM) showed satis-
  factory performance in a 25 cm^2 cell for over 1000 hours.

Materials Evaluation

- Corrosion resistance tests of phenolic resins at 191°C
  have shown that Novolak and Resol resins slowly etch
  in phosphoric acid.

- Cresol modified phenolics decompose rapidly in 185°C
  acid.

- Resistivities of molded resin/graphite mixtures decrease
  more than 50% by lowering the resin content from 32% to
  22%.

- Compression of cell components at 40 to 60 psi (270 to
  410 kPa) decreases the resistivity by a factor of 10.

Endurance Testing

- Estimates of acid loss using analytical expressions

ENERGY RESEARCH CORPORATION

> (Margules, van Laars, and Wilsons equations) have not
> been satisfactory to date.
>
> ● Data from the first acid loss experiment showed the
> P_4O_{10} vapor concentration to be 2 ppm at 191°C and
>   103 wt% acid.
>
> ● Compression experiments showed that the backing paper
>   can become wettable by overcompression of a stack.
>   This may be an important factor in the increase of dif-
>   fusion resistance as a function of time.

Short-Stack Testing

> ● Five 1200 cm² cell stacks have been tested, with pro-
>   gressively better results. Acid management in these
>   stacks needs further improvements.
>
> ● A temperature map of a 1200 cm² cell stack has been
>   obtained. The results indicate the need for an im-
>   proved temperature profile via proper insulation and
>   preheating of gases.

ENERGY RESEARCH CORPORATION

TABLE OF CONTENTS

ENERGY RESEARCH CORPORATION

LIST OF FIGURES

ENERGY RESEARCH CORPORATION

LIST OF TABLES

ENERGY RESEARCH CORPORATION

TASK I.   COMPONENT DEVELOPMENT

1.1   Matrix Development

Previously, electrodes have been sintered prior to being coated with SiC matrices, because the electrodes and matrices were sintered at different temperatures. Recent tests have indicated that electrodes can perform well after being sintered at lower than normal temperatures, while SiC matrices are stronger and appear to wick adequately after being sintered at higher than normal temperatures. Since the two temperatures have drawn closer together, it would seem feasible to combine the two sintering operations. Not only would time and handling be saved, but by sintering the matrix and the electrode together, a more intimate contact between the two might be achieved, re- sulting in improved handleability and better wetting of the electrode.

To test this idea, an unsintered electrode was coated with SiC and then sintered for 40 minutes at 225°C, followed by 25 minutes at 350°C. The electrode-matrix combination was used in Cell No. 1294 (Table I.1). The cell started up well and is still running near peak performance. The matrix does seem to offer improved handleability. If stressed to the point where some SiC flakes off, the matrix appears to shear internally, leaving a layer of SiC firmly attached to the electrode rather than separating at the matrix-electrode interface.

Another way to improve the handleability of the matrix is to increase the amount of plastic in the inking vehicle. Since the primary purpose of the inking vehicle is to control the viscosity of the SiC slurry, the concentration of the plas- tic cannot be varied indiscriminately. By using a lower molecu- lar weight grade of the same plastic, a solution can be produced with the same viscosity, but with six times the concentration of the material presently used. Matrices produced with the

DEN3-67

TABLE I.1

TESTING SUMMARY OF 25 cm² CELLS

CELL NO.	1278	1279	1287	1294
TEST OBJECTIVE	Backing Test	Matrix	Backing	Matrix & Electrode Sintered Together
CELL CHARACTERISTICS				
ANODE				
TYPE	Rolled	Sheet Mold	Rolled	Rolled
% TFE	40%	40%	40%	40%
LOADING, mg Pt/cm²	0.3	0.2	0.3	0.3
CATHODE				
TYPE	Rolled	Rolled	Rolled	Rolled
% TFE	40%	40%	40%	40%
LOADING, mg Pt/cm²	0.5	0.5	0.5	0.5
MATRIX	SiC	SiC	SiC	SiC
% TFE	4%	2%	4%	4%
POROSITY	33%	---	---	---
THICKNESS, cm	0.015	0.007	0.006	0.007
SINTERING	25 min. @ 275°C	15 min. @ 350°C	25 min. @ 275°C	40 min. @ 225°C 25 min. @ 350°C
ANODE BACKING, % FEP	20%	37%	32%	39%
CATHODE BACKING, % FEP	40%	39%	40%	36%
PERFORMANCE IR FREE				
AIR @ 100 mA/cm²				
PEAK mV	723	730	705	715
AVERAGE mV	710	720	685	705
PRESENT mV	600 (@ 200 mA/cm²)	*	610 (@ 200 mA/cm²)	705
AIR @ 200 mA/cm²				
PEAK	670	640	650	645
O₂ @ 100 mA/cm²	780	770	775	775

*Test Terminated

higher concentration inking vehicle are strong enough to be
cut to size with a steel rule die and can be handled without
SiC rubbing off. The porosity of these matrices after sinter-
ing is high (68%) and the bubble pressure is good (131 kPa,
19 psi).

1.2   Component Scale-up

Preparing SiC slurries in single matrix batches is a time-
consuming operation. A large batch of SiC (enough for approxi-
mately fifteen 350 cm^2 or five 1200 cm^2 matrices) was prepared
with a ball mill in little more than an hour. Optimization of
the milling conditions has yet to be performed, but the tech-
nique appears suitable for the preparation of large batches of
SiC slurry.

A number of 1200 cm^2 electrodes have been prepared on a
sheet mold. Initially there were problems with the uniformity
of the deposited catalyst layer, but these have been resolved
and the sheet mold technique can now consistently produce good
quality electrodes.

1.3   Definition and Control of Electrolyte Volume Changes

Two techniques which can be used to produce selectively
wetproofed backings have been identified. These techniques
result in backings that are completely wetproofed on one side
(the gas side) and are spotted with wetproofed areas on the
other (catalyst) side. The backing then becomes an acid in-
ventory control member (AICM) which can be used to store or
give up electrolyte as the running conditions of the cell dic-
tate. The amount of backing area which must remain nonwettable
in order to ensure a proper supply of gas to the cell is still
being resolved.

Another way to produce an AICM is to reduce the amount
of FEP in the backing, making it partially wettable over its

ENERGY RESEARCH CORPORATION

entire surface. In order to test this idea, a 25 cm² cell was
built with an anode backing containing approximately half the
FEP normally used. The cell (No. 1278, Table I.1) ran well
for over 1000 hours and has slowly begun to show signs of de-
cay. These results are encouraging and will be evaluated fur-
ther.

Tests are being conducted to determine the maximum amount
of acid that can be absorbed by various cell components as well
as the amounts they are likely to pick up under cell assembly
and test conditions. Table I.2 lists a number of electrode com-
ponents and the amount of acid they absorbed after 20 hours of
being float-filled at 177°C. The acid pickup represents the
average of two tests on each sample. The deviation between the
two tests was small. The float filling technique probably in-
dicates the maximum amount of acid that can be absorbed by a
component without applying external pressure to the acid.

Another technique for determining the acid absorption ca-
pacity of electrodes is to wick them from a matrix, as is done
during cell assembly. In this method, a phenolic fiber matrix
is soaked in hot acid and then placed between two electrodes.
The sandwich is then compressed and placed in an oven at 177°C.
The amount and rate of acid absorption can be determined by
periodically weighing the electrodes. Tests of this kind are
presently being conducted.

1.4   Bipolar Plate Technology

Post-curing of bipolar plates to promote cross-linking of
the resin binder was investigated. Bipolar plates were heat-
treated in air at various rates to 210°C. During post-cure,
gases are evolved and blistering of the plates occurs if the
temperature increases too rapidly.

Experiments were conducted on sections (13 cm x 13 cm x
0.4 cm) of 13 cm x 38 cm bipolar plates with a programmable

TABLE I.2

ACID PICK-UP OF ELECTRODES AND BACKINGS

	SAMPLE		THICKNESS, CM	ACID PICK-UP, CM^3 OF ACID/CM^2 OF SAMPLE
1.	ELECTRODE ON STACKPOLE	0.7 MG-PT/CM^2	0.053	5.48×10^{-3}
1A.	ELECTRODE	0.7 MG-PT/CM^2	0.023	5.48×10^{-3}
2.	ELECTRODE ON KUREHA	0.3 MG-PT/CM^2	0.048	3.35×10^{-3}
2A.	ELECTRODE	0.3 MG-PT/CM^2	0.013	4.12×10^{-3}
3.	STACKPOLE	35% FEP PICK-UP	0.041	0.69×10^{-3}
4.	KUREHA	45% FEP PICK-UP	0.048	3.07×10^{-3}
5.	STACKPOLE	26% FEP PICK-UP	0.048	2.92×10^{-3}
6.	KUREHA	27% FEP PICK-UP	0.046	2.92×10^{-3}
7.	STACKPOLE	NO FEP	0.046	32.7×10^{-3}
8.	KUREHA	NO FEP	0.046	26.0×10^{-3}
9.	KYNOL MATRIX		0.047	40.4×10^{-3}
10.	SIC 125 (4% TFE)		0.015 SIC	13.1×10^{-3}

SINTERED 25 MIN. @ 275°C
ON AN ELECTRODE (0.54 MG PT/CM^2)

temperature controller. The plates were inspected before and
after post-cure for observable blisters. Table I.3 demonstrates
the effect of three different post-cure cycles on the bipolar
plates.

Low resin bipolar plates (13 cm x 38 cm) were fabricated
with 75% A-99 Graphite/25% Colloid 8440. To achieve dimensional
tolerances, the weight of the plates was increased 12.5 %.
Satisfactory plates were produced by this process.

Molding trials with 25 wt% Varcum 24-655 were initiated
for 13 cm x 38 cm bipolar plates. Initial results indicate that
the resin content can be lowered to 25% without appreciable dif-
ficulty.

TABLE I.3

BIPOLAR PLATE POST-CURE CYCLES

HOURS 20°C TO 210°C	NUMBER OF BLISTERS	AVERAGE DIAMETER OF BLISTERS cm	RATE, °C/hr						
			TEMPERATURE RANGE, °C						
			20-160	160-170	170-180	180-190	190-200	200-210	210-220
11.7	0	–	60	5	5	5	5	5	5
4.8	3	<0.2	60	20	20	20	20	20	20
1.8	12	<0.2*	120	120	120	60	60	60	–

Note: Plate Composition – 67% Graphite/33% Colloid 8440

       Plate Size – 13 cm x 13 cm x 0.4 cm

*Blisters with surface cracking

TASK II.   MATERIAL EVALUATION

2.1   Component Corrosion Resistance

Table II.1 lists the weight and thickness changes of 100%
resin samples and graphite/resin composite samples which were
soaked in pots of 191°C phosphoric acid. The surfaces of near-
ly all the 100% resin samples were etched. Initial microscopic
examination of the samples using both optical and scanning elec-
tron microscopes indicated that a selective etching had occurred.
The reason for the selective etching is to be determined.

2.2   Physical Property Measurements

Flow Test

Preformed disks of graphite/resin (5.7 cm diameter and
35 grams in weight) were compressed between flat steel plates
in order to evaluate their flow characteristics. After press-
ing to a set pressure, disk thickness and diameter were found
to be dependent on the wt% resin and the temperature of the
steel plates. Based on the assumption that the flowability
of the composites is inversely proportional to the thickness
at the center of the pressed disk, a flow index was defined
and calculated:

$$f = \frac{0.05}{T}$$

Where,

   f = Flow index

   T = Thickness (inches)

Figures II.1 and II.2 are plots of temperature versus flow
indices for four graphite/resin compositions. The maximum
flow for Varcum 24-655 (S-18464) occurs between 130°C and

ENERGY RESEARCH CORPORATION

TABLE II.1

CORROSION OF GRAPHITE/RESIN

Resin	100% Resin Material		Graphite/Resin Material	
	Δ% Weight	Δ% Thickness	Δ% Weight	Δ% Thickness
Colloid 8440	+1	+1	+2	0
Varcum 24-655	-3	-1	0	-1
H-Resin H-A43	-6	-4	0	-1
Varcum 29703	-3	-3	-	-
Varcum 29319	-2	0	-	-
Plenco 402	-2	-1	-	-
Plenco 653	Sample Disintegrated After 100 Hours		-	-
Plenco 956	-2	-1	-	-
Xylok 225	-8	-8	-	-
Radel	0	0	-	-

NOTE: Wt% Resin in graphite/resin samples was between 22 and 32%.

*Test duration in H_3PO_4 ranged between 1100 to 1600 hours at 177°C.
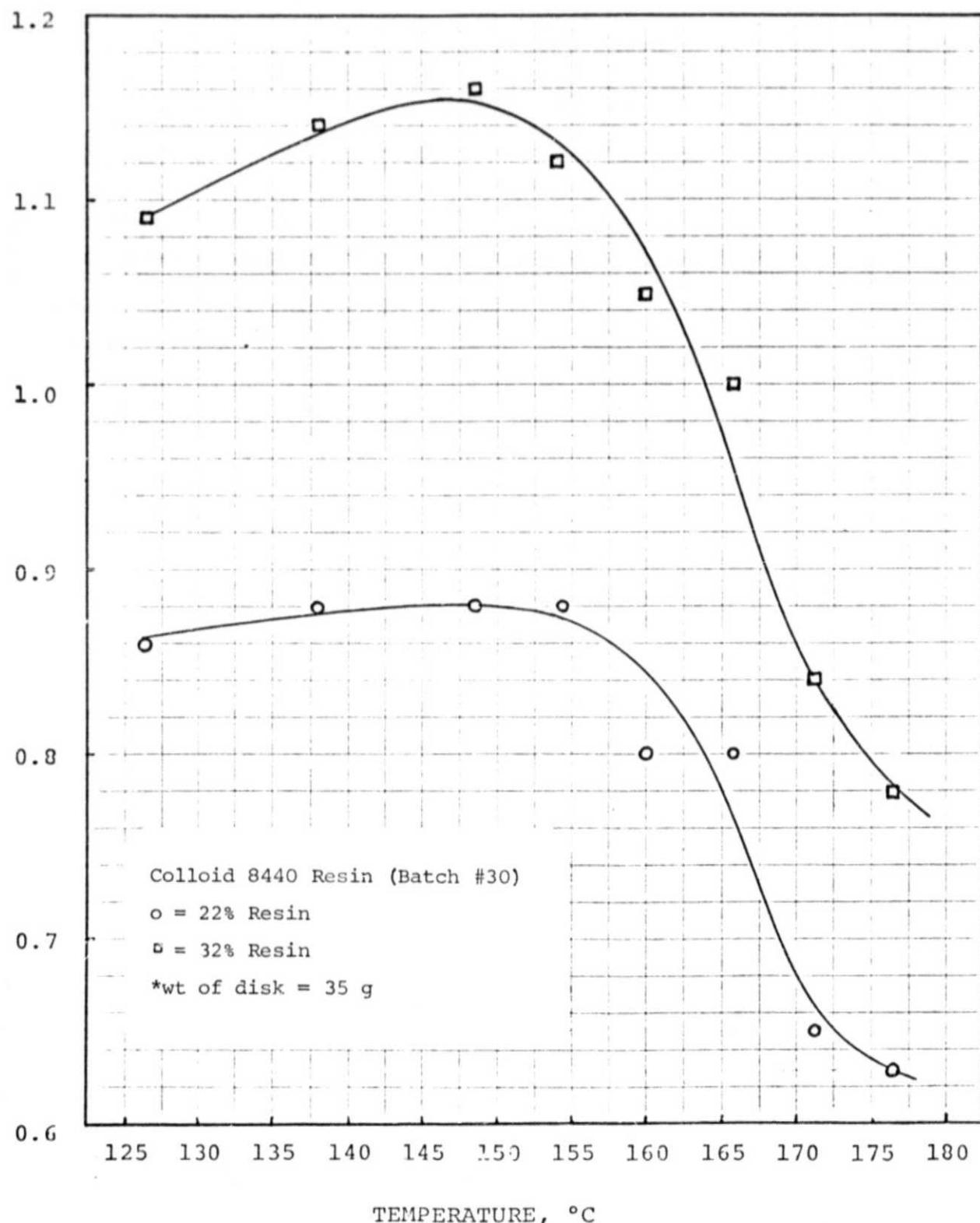
FIGURE II.1   FLOW VARIATIONS OF A-99 GRAPHITE/COLLOID RESIN
VS TEMPERATURE
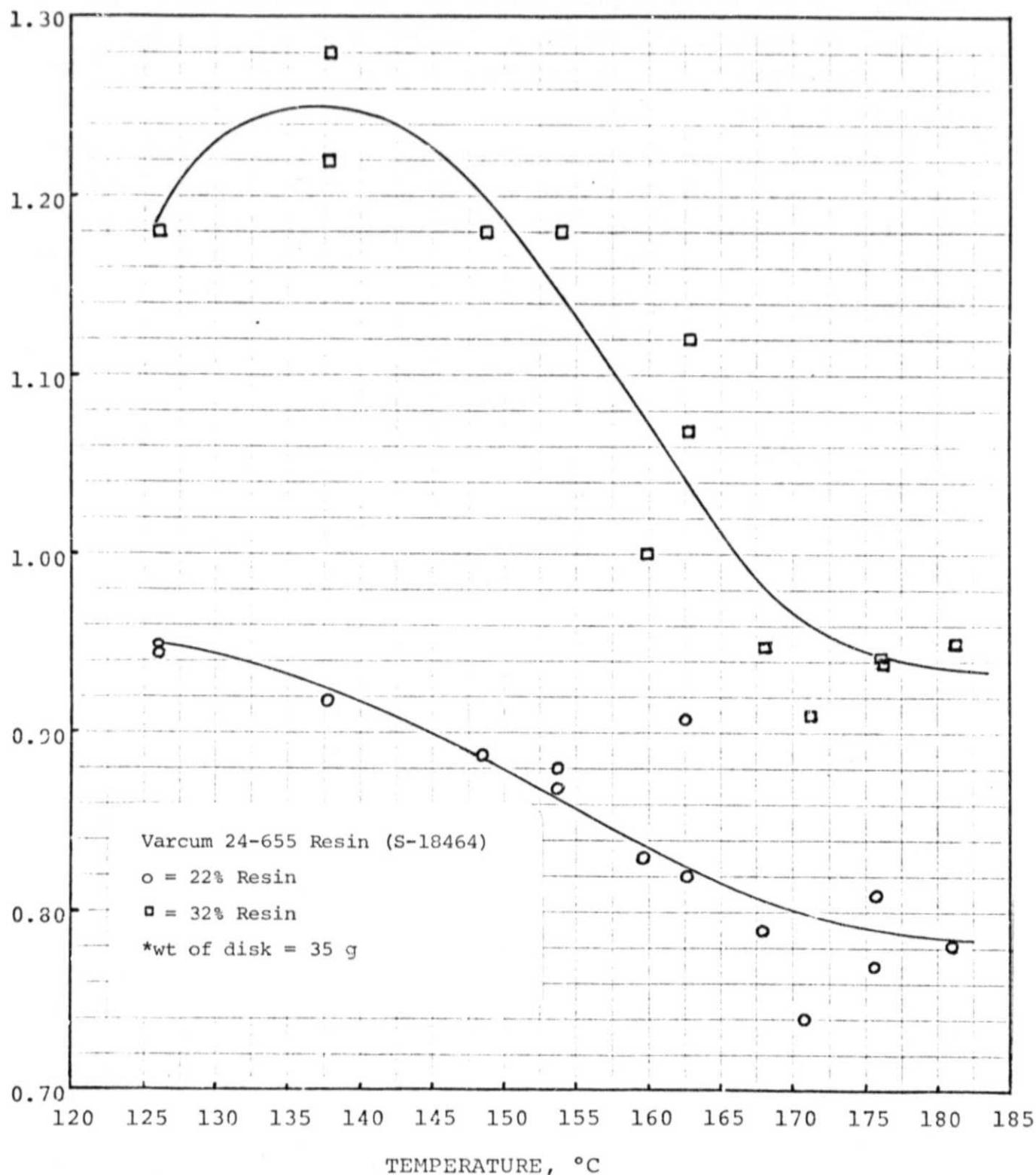
FIGURE II.2   FLOW VARIATIONS OF A-99 GRAPHITE/VARCUM RESIN
VS TEMPERATURE

145°C, and for Colloid 8440 (Batch No. 30) between 140°C and
155°C. At temperatures below 130°C, the composite materials
were thermoplastic, requiring cooling under pressure to achieve
a uniform, dense material.

Changes in the amounts and types of graphite or resin also af-
fect the flow which decreased with decreasing wt% resin. Addition
of flake graphite (Asbury 850) while maintaining a constant wt%
resin increases the flow. For example, substituting the standard
graphite with a flake graphite (Asbury 850), the flow index in-
creased ∿ 11%.

The above flow tests were made using flat steel plates as
dies. The effect of ribbed plates on the flow was also investi-
gated. A flow test using two ribbed plates did not yield a cir-
cular disk after pressing. The graphite/resin tends to flow in
the direction of the ribs, which distorts the former circular
pattern obtained between flat steel plates. The amount of flow
was not observed to decrease due to the ribbed dies, but the
direction of flow was changed.

2.3   Resistivity Measurements

Figure II.3 is a plot of resistivity of graphite/resin com-
posites with Varcum 24-655 (S-18464) and Colloid 8440 (Batch
No. 30) resins. A four point method was used to measure the
voltage drop across cylindrical samples. The resistivity of
the graphite/resin composites more than doubled by increasing
the resin content from 22 to 32 wt%.

Resistivities of composites with Varcum 24-655 resin were
consistently less than the composites with Colloid 8440 resin.

Measurement of the electrical resistivity of various cell
components indicates that the electrical resistivity of these
materials is greatly dependent on their state of compression.

There are two basic reasons for this dependence: a) con-
tact resistance, and b) compressibility. As compression
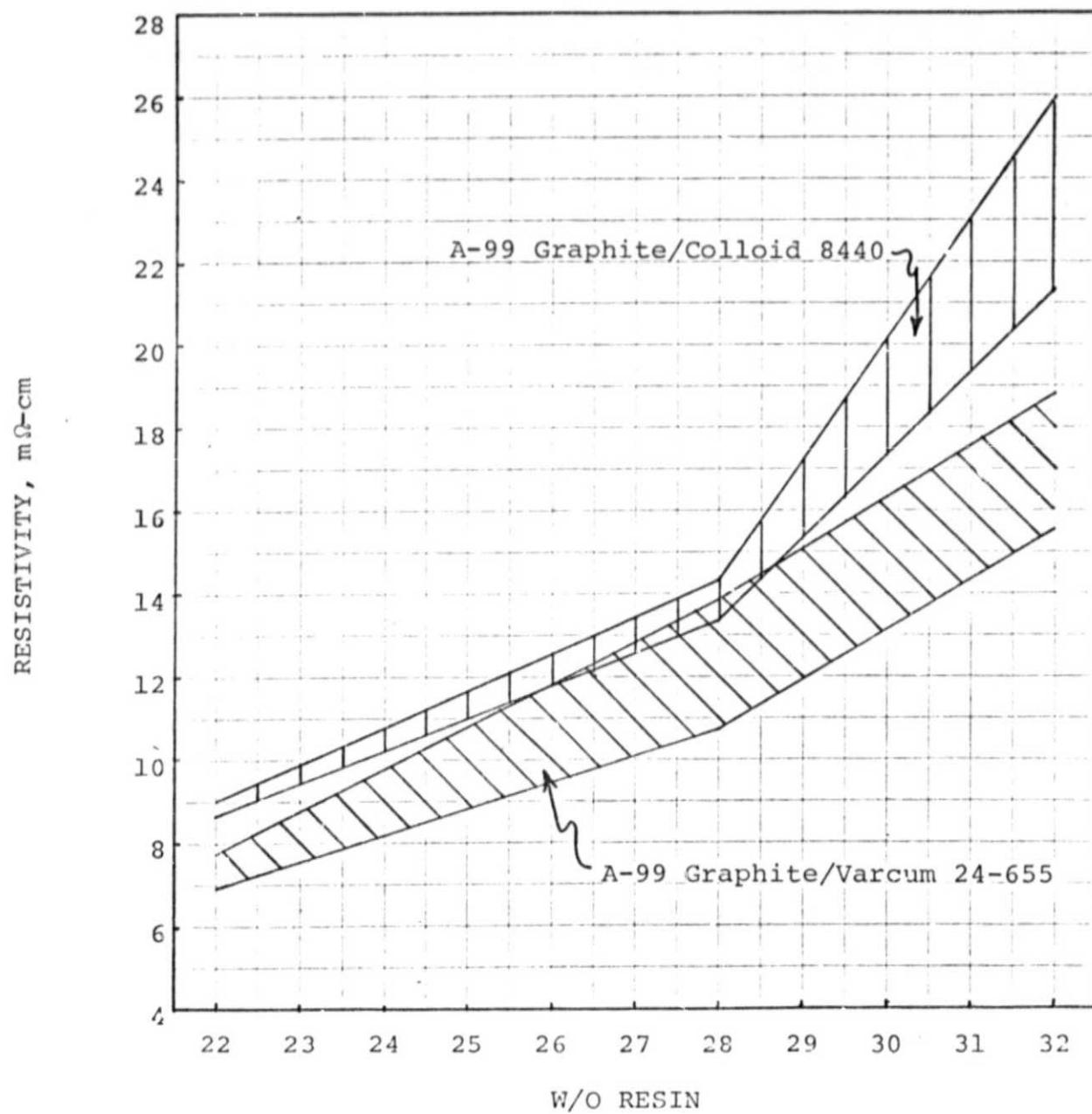
FIGURE II.3   RESISTIVITY OF GRAPHITE/RESIN

increases, both of these factors result in a lower resistivity.
Figure II.4 illustrates the amount of compression sustained by
electrode components in one series of tests. Presently ERC
stacks are built with 300 to 500 kPa (44 to 73 psi) compression.
Figure II.4 shows the drop in resistivity produced by compres-
sion of cell components. The data in Figure II.5 demonstrates
the compressibility of each component. Both factors are chang-
ing simultaneously and result in a rapid change of resistivity
at very low compressive loads. In addition to the resistivity
measurements shown, tests were performed on an electrode coated
with a SiC matrix. The tests indicate that the matrix is a good
insulator.

2.4   Density Measurements

Densities of samples cut from pressed 10 cm x 10 cm plates
and from flow test specimens were measured before and after post-
cure (see Table II.2). The densities decreased after post-cure
and also decreased with increasing resin content as expected.
The post-cure heat treatment consisted of the following steps:

1.   146°C for 2 hrs.

2.   182°C for 2 hrs.

3.   204°C overnight

The final density also seemed to be affected by the age of
the starting resin. Samples prepared from 1 month old resin had
a lower density after post-cure than those prepared from 5 month
old resin.
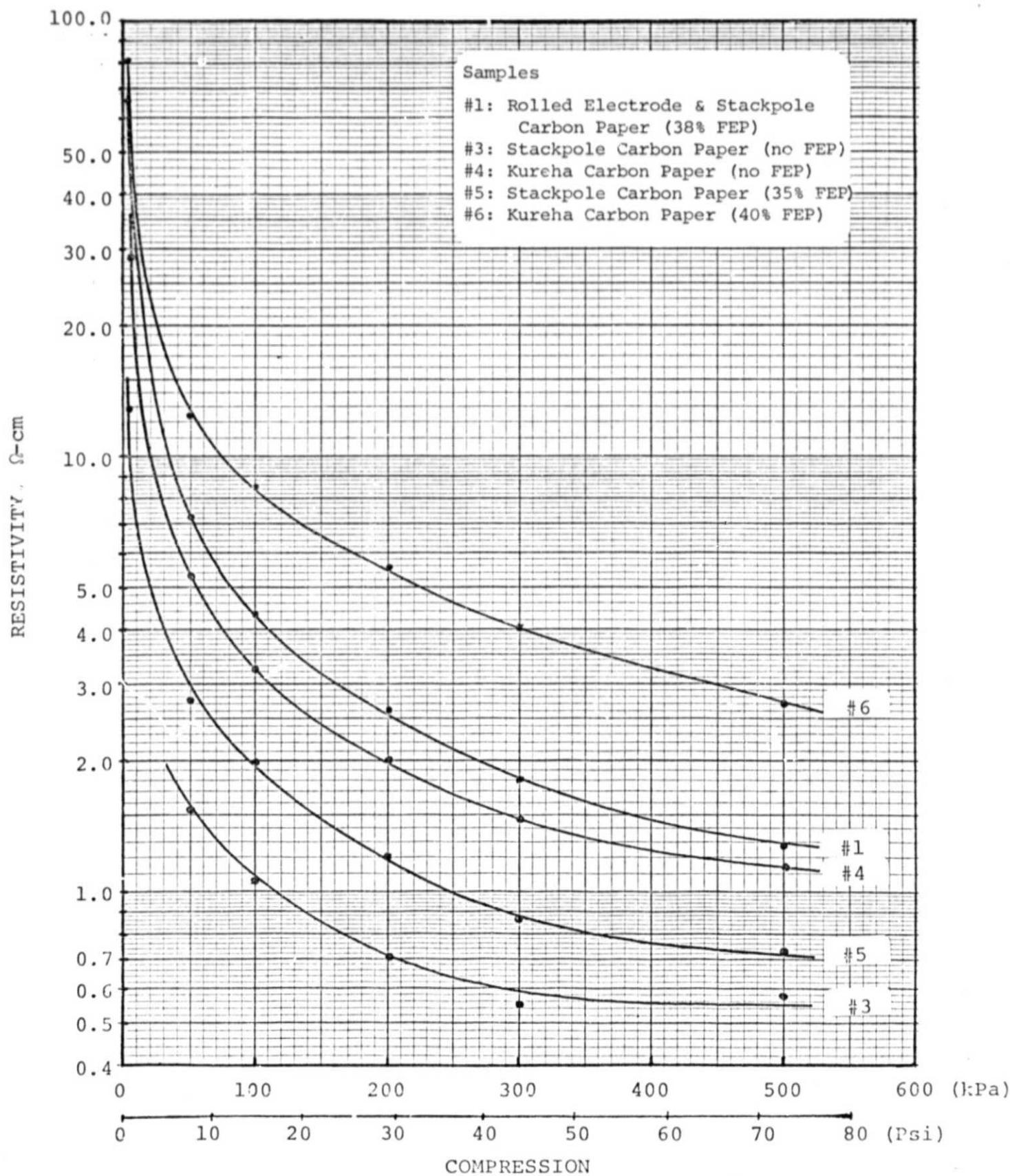
FIGURE II.4   VARIATION OF CELL COMPONENT RESISTIVITY
AT DIFFERENT PRESSURES

D0483
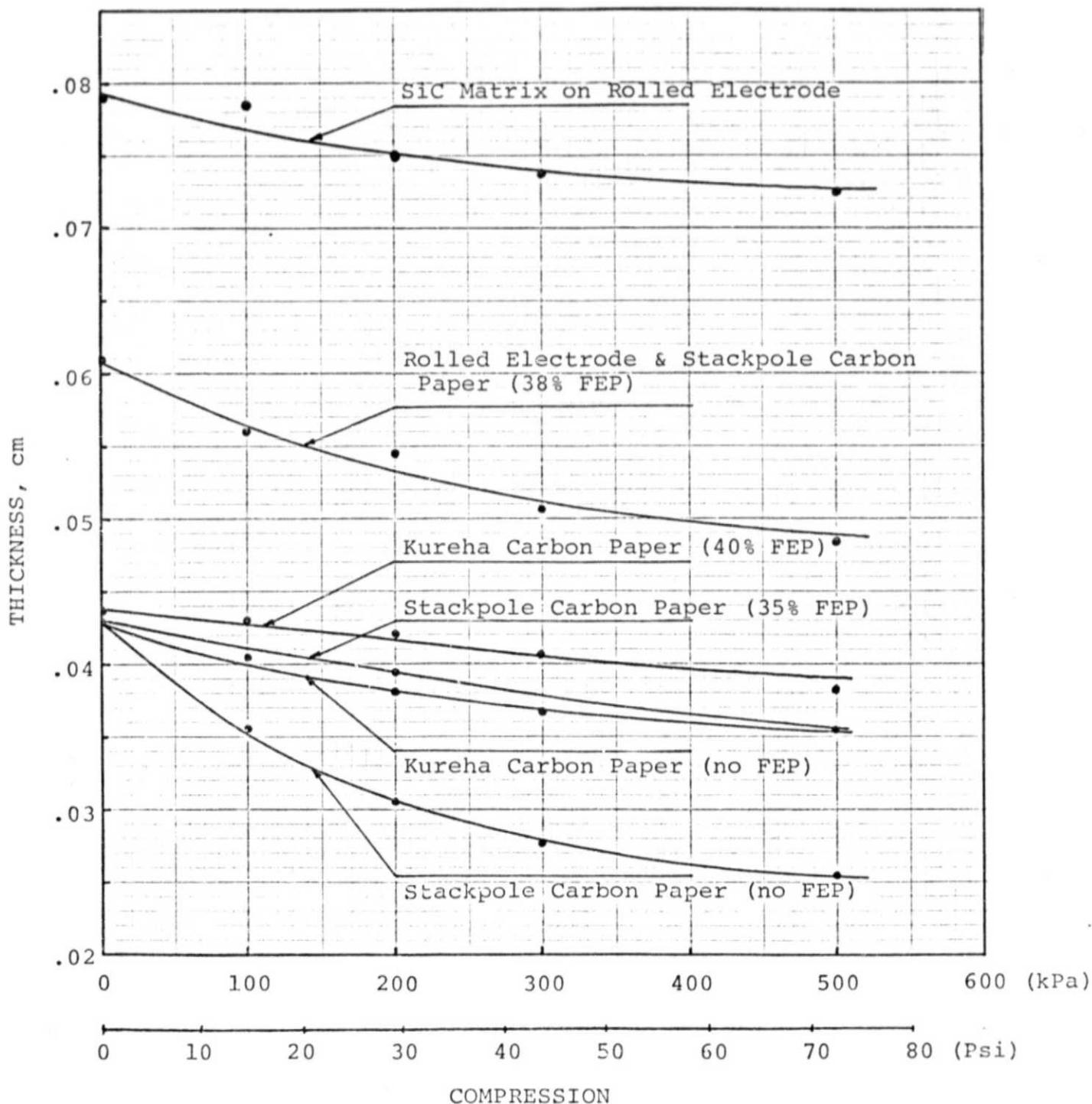
FIGURE II.5   VARIATION OF CELL COMPONENT THICKNESS
AT DIFFERENT PRESSURES

D0484

TABLE II.2 DENSITY MEASUREMENTS

RESIN	RESIN CURE DENSITY, g/cc		COMPOSITION		SAMPLE ORIGIN	NUMBER OF SAMPLES	DENSITY, g/cm³		
	VENDOR	IN-HOUSE	W/O GRAPHITE W/O RESIN	V/O GRAPHITE* V/O RESIN			THEORETICAL * AFTER POST-CURE	BEFORE POST-CURE	AFTER POST-CURE
H-RESIN (H-A43)	1.12 to 1.13	1.15	78/22	64/36	4" x 4" PLATE	22	1.86	1.81	1.79
			78/22	64/36	FLOW TEST	2	1.86	1.81	1.77
			72/28	57/43		2	1.77	1.77	1.71
			68/32	52/48		2	1.72	1.73	1.66
COLLOID 8440 (rec'd 6/78)	1.30 to 1.32	1.25	78/22	66/34	4" x 4" PLATE	6	1.91	1.90	1.83
			78/22	66/34	FLOW TEST	2	1.91	1.90	1.81
			72/28	59/41		2	1.84	1.85	1.78
			68/32	54/46		2	1.79	1.81	1.75
VARCUM 24-655 (rec'd 7/78)	1.25 to 1.27	1.25	78/22	66/34	4" x 4" PLATE	4	1.91	1.91	1.88
			78/22	66/34	FLOW TEST	2	1.91	1.92	1.82
			72/28	59/41		2	1.84	1.82	1.78
			68/32	54/46		2	1.79	1.81	1.75
VARCUM 24-655 (rec'd 11/78)	1.25 to 1.27	1.17	78/22	65/35	FLOW TEST	2	1.87	1.92	1.81
			72/28	57/43		2	1.79	1.85	1.69
			68/32	52/48		2	1.74	1.80	1.67

* Calculated using densities for 100% resin sample measured in-house, and a density of graphite equal to 2.25 g/cm³

ENERGY RESEARCH CORPORATION

TASK III.   ENDURANCE TESTING

  3.1   Evaluation of Acid Loss

  In the last quarterly report, the partial pressure of
H_3PO_4 was predicted as a function of temperature, neglecting
the effect of acid concentration. An effort was made during
this quarter to include the effect of acid concentration.

  A binary system of P_4O_{10} and H_2O with an ideal gas phase
and non-ideal liquid phase was assumed. Estimation of partial
pressures in the gas phase requires a knowledge of liquid phase
activity coefficients.

$$P_A = \gamma_A \, P_A \, x_A \qquad\qquad\qquad (III.1)$$

Where,

  P_A = partial pressure of component A

  γ_A = activity coefficient of A in the liquid phase

  P_A = vapor pressure of pure A

  x_A = mole fraction of A in the liquid phase

Various correlations are available for the estimation of liquid
phase activity coefficients, e.g., van Laars, Margules, and
Wilson equations. These equations were evaluated using the
available vapor-liquid equilibrium data* at atmospheric pressure.

  Margule Equations

  The two parameter Margule equations[†] are presented below:

---

*Brown, E. H., Whitt, C. D.; "Vapor Pressure of Phosphoric Acids", Industrial
 and Engineering Chemistry, Vol. 44 No. 3, March 1952, pp. 615.

[†]Reid, R. C., Prausnitz, J. M. and Sherwood, T. K., "The Properties of Gases
 and Liquids", third edition, McGraw-Hill Book Company, pp 300, 1976.

ENERGY RESEARCH CORPORATION

$$\ln \gamma_A = C_1 \, x_B^2 + C_2 \, x_B^3 \qquad\qquad (III.2)$$

$$\ln \gamma_B = (C_1 + 3/2 \, C_2) \, x_A^2 - C_2 \, x_A^3 \qquad (III.3)$$

Where,

A,B = Margule constants

Vapor-liquid equilibrium data at 225°C and 255°C was used to estimate the constants listed in Table III.1. In the estimation of these constants, the vapor pressure of pure P_4O_{10} was obtained by extrapolating the vapor pressure data of the liquid H-form of P_4O_{10}.

TABLE III.1

MARGULES CONSTANTS

Temperature*, °C	Margules Constants	
	C_1	C_2
225	-419	474
255	284	-339

The wide variation of constants with temperature indicated that Margules equations did not fit well. This may be attributed to the considerable non-symmetry of the system[†].

Van Laar equations[‡] are also two parameter equations and are presented below.

---

*Temperature at which experimental vapor-liquid equilibrium was measured by Brown and Whitt, cited

[†]Perry, J. H. (editor), Chemical Engineers' Handbook, third edition, McGraw Hill Book Company, Inc., 1950, pp 527.

[‡]Reid, R. C., et al, op cit.

ENERGY RESEARCH CORPORATION

$$\ln \gamma_A = \frac{a}{\left(1 + \frac{a}{b} \frac{x_A}{x_B}\right)^2} \qquad\qquad \text{(III.4)}$$

$$\ln \gamma_B = \frac{b}{\left(1 + \frac{b}{a} \frac{x_B}{x_A}\right)^2} \qquad\qquad \text{(III.5)}$$

Where,

   a, b = van Laar constants

The constants computed from the vapor-liquid equilibrium data
are listed in Table III.2.   The vapor pressure of pure P_4O_{10}
was estimated using correlations for both the solid and the
liquid H forms.   With these constants, P_4O_{10} vapor concentra-
tions were predicted at a fuel cell operating condition (191°C
and 99.5 wt % acid) and tabulated.   The following observations
were made from Table III.2:

- The van Laar constants varied with temperature.

- Use of vapor pressure correlation for solid H form
  resulted in lower P_4O_{10} vapor concentrations than
  for liquid H form.

- The van Laar constants evaluated from vapor-liquid
  equilibrium data at lower temperatures yielded higher
  P_4O_{10} vapor concentrations.

- The van Laar constants evaluated from extrapolation
  of equilibrium data to 188°C predicted almost 9
  times larger P_4O_{10} vapor concentrations than the ex-
  perimental data*.

---

*United Technologies, Power Systems Division, South Windsor, CT, "Improvement
of Fuel Cell Technology Base", _Technical Progress Report, No. 3_, prepared for
U. S. Department of Energy, under Contract ET-76-C-03-1169, June 1978.

TABLE III.2

P_4O_{10} VAPOR CONCENTRATIONS USING VAN LAAR EQUATIONS

No.	Temperature[†], °C	VAPOR PRESSURE OF PURE P_4O_{10} 10^2 N/m² (mm Hg)		Van Laar Constants		P_4O_{10} VAPOR CONCENTRATION ESTIMATED at 191°C & 99.5% acid concentration ppm by volume
		SOLID H FORM	LIQUID H FORM	a	b	
1	302	161.6 (121.2)	–	-162.5	-5.13	0.60
2	255	28.0 (21.0)	–	-145.0	-5.40	1.25
3	255	–	122.8 (92.1)	-125.0	-6.00	3.08
4	225	7.3 (5.5)	–	-129.4	-4.79	2.24
5	225	–	47.2 (35.4)	-109.0	-5.50	4.49
6*	188	1.2 (0.9)	–	- 91.4	-4.44	4.26
7*	188	–	12.8 (9.6)	- 86.6	-4.82	7.24

*From extrapolated vapor liquid equilibrium data.

[†]Temperature at which experimental vapor-liquid equilibrium was measured by Brown and Whitt, op cited.

ENERGY RESEARCH CORPORATION

- Vapor-liquid equilibrium data at 302°C yielded van Laar constants which predicted P_4O_{10} vapor concentration close to the experimental data* (25% higher than experimental).

The variation of predicted values might to some extent be attributed to: 1) the use of equilibrium data covering a wide range of temperatures, and 2) the nonsymmetry of the system . (system with one constant more than double the other can be said to be widely nonsymmetrical).

Wilson Equations

Wilson equations[†] are more complicated than the previous two kinds but are still two parameter equations. They can be written as:

$$\ln \gamma_A = -\ln \left(x_A + C_3 x_B\right) + x_B \left[\frac{C_3}{x_A + C_3 x_B} - \frac{C_4}{C_4 x_A + x_B}\right] \quad (III.6)$$

$$\ln \gamma_B = -\ln \left(x_B + C_4 x_A\right) - x_A \left[\frac{C_3}{x_A + C_3 x_B} - \frac{C_4}{C_4 x_A + x_B}\right] \quad (III.7)$$

Where;

   C_3, C_4 = Wilson parameters

Equilibrium data at 255°C, 225°C and 191°C were used to estimate the parameters. The P_4O_{10} vapor concentrations predicted using these parameters are listed in Table III.3 from which the following observations were made:

- Wilson equation parameters varied with temperature.
- Parameters evaluated from vapor-liquid equilibrium

*United Technologies, op cit

[†]Reid, R. C., et al, op cit

TABLE III.3

P_4O_{10} VAPOR CONCENTRATIONS USING WILSON EQUATIONS

No.	Temp., °C	WILSON PARAMETERS		P_4O_{10} VAPOR CONCENTRATION ESTIMATED AT 191°C & 99.5% ACID CONCENTRATION ppm by volume
		C_3	C_4	
1	302	1.0266	1030.5	0.98
2	255	0.6963	598.6	1.30
3	225	0.3927	393.6	1.90
4	188	0.1142	219.0	3.05

ENERGY RESEARCH CORPORATION

data at the fuel cell operating temperature (188°C)
still result in high P_4O_{10} vapor concentrations
(almost six times greater than the experimental
value).

● The use of vapor-liquid equilibrium data at 302°C
yielded parameters which predicted lower P_4O_{10} vapor
concentrations but still twice the experimental value.

Conclusions

The following conclusions were made from this evaluation
of various correlation equations:

● Margules equations are not applicable to the present
system.

● The van Laar equations predict P_4O_{10} concentrations
closer to the experimental data than Wilson equations.

● Use of vapor-liquid equilibrium data at higher tem-
peratures predicted P_4O_{10} concentrations closer to
the experimental value. This may be due to the ac-
curacy of the equilibrium data since, at higher tem-
peratures, P_4O_{10} concentration is easier to measure.

3.2   Experimental Measurement of Acid Loss

An experiment for measurement of acid loss from a fuel
cell was conducted. A small size (25 cm²) cell was run at 191°C
with 510 cm³/min of air flow (5 stoich based on 215 mA/cm²) on
each side. The air was humidified at room temperature. The
acid vapor picked up by the air was trapped by the steel wool
in the adsorber tubes attached to the exit of the fuel cell.

After approximately 620 hours, air flow rates from the ad-
sorbers were measured. It was found that the anode side flow
increased to 895 cm³/min, whereas cathode side flow decreased
to 107 cm³/min. Flow rates at the cell inlet and exit were

also measured. Because a crossleak in the cell was suspected, the experiment was terminated, and the cell components were analyzed for acid loss.

The cell component weights before and after the test showed an acid loss of 1.204 gms (102 wt% H_3PO_4) in 620 hours. The P_4O_{10} vapor concentration in the exit air was computed to be 2 ppm (by volume). The acid concentration in the cell during the experiment was estimated to be 103 wt%.

To provide a check for the above method of determining acid loss, adsorber weight measurements before and after the test were taken. A weight increase of 0.641 gm was observed in 528 hours of the operating period. Assuming the weight gain is solely due to the formation of $Fe_3(PO_4)_2$, a P_4O_{10} vapor concentration of 1.3 ppm was estimated in the exit air.

The variation in concentration values from cell component weights and adsorber weights may be attributed to some operational difficulties experienced during the test. Similar experiments are being carried out to verify the results obtained.

3.3 Stack Testing

Stack testing of 350 cm^2 stacks during this quarter is summarized in Table III.4. Testing performed this quarter can be divided into the following:

A.   Tests in support of scale-up stacks

B.   Effect of operating conditions

C.   Component evaluation in stacks

A.   Tests in Support of Scale-up Stacks

Several tests have been designed to analyze problems encountered in 1200 cm^2 stacks.

TABLE III.4   STACK TESTING SUMMARY

- Short Stacks (350 cm^2)
- 108 ASF (40 A)

STACK NO.	339			341			347			348		
TEST OBJECTIVE	Operational Variables			SRF Testing Endurance			Freezing Humidification			No Tantalum		
NO. CELLS	3			3			3			3		
ANODE mg Pt/cm^2	.61	.58 Std	.60	.30	.31 Std	.29	.58	.61 Std	.55	.54	.51 Std	.56
CATHODE mg Pt/cm^2	.91	.92 Std	.98	.60	.58 Std	.60	.87	.89 Std	.96	.87	.84 Std	.94
MATRIX	Kynol			Kynol			Kynol			Kynol		
PLATE/CONDITION	Good			Good			Good			Good		
PEAK PERFORMANCE, volts — Air- / OCV-	.62 .81	.61 .81	.66 .87	.60 .81	.61 .85	.58 .81	.60 .86	.62 .84	.63 .86	.59 .83	.60 .83	.59 .84
PRESENT PERFORMANCE, volts — Air- / OCV-							.56 .82	.57 .89	.62 .90			
O$_2$ GAIN, volts	.05	.08	.09	.08	.05	.07	N/A			.06	.06	.06
MΩ READING	4.5			5.1			N/A			4.95		
ACID HISTORY							Res. Removed at 1985 hrs.					
GAS UTILIZATION/ SENSITIVITY							Air Sensitive					
TOTAL HOURS	3945			3822			Life Test: 2733 Freezer: 657 Cycles: 9			2780		
REMARKS	Disassembled			Disassembled						Disassembled		

TABLE III.4   STACK TESTING SUMMARY

- Short Stacks (350 cm^2)
- 108 ASF (40 A)

STACK NO.	349			351			352			353		
TEST OBJECTIVE	High Current Density Endurance			SiC			SRF Testing Humidification			Horizontal		
NO. CELLS	3			3			3			3		
ANODE mg Pt/cm^2	.54	.58 Std	.55	.29	.32 Std	.26	.28	.29 Std	.27	.62	.57 Std	.51
CATHODE mg Pt/cm^2	.94	.96 Std	.90	.53	.49 Std	.62	.62	.61 Std	.64	.82	.86 Std	.86
MATRIX	Kynol			SiC			Kynol			SiC		
PLATE/CONDITION	Fair			Good			Good			Good		
PEAK PERFORMANCE, Air-OCV- volts	.61 .82	.62 .84	.61 .85	.58 .72	.61 .80	.58 .72	.60 .84	.60 .84	.60 .85	.60 .77	.60 .71	.59 .78
PRESENT PERFORMANCE, Air-OCV- volts	.56 .82	.58 .85	.56 .82				.56 .81	.57 .84	.54 .82			
O$_2$ GAIN, volts	.06	.06	.07	N/A			.07	.07	.09	.11	.07	.13
MΩ READING	5.0			N/A			5.8			4.8		
ACID HISTORY	Res. Removed at 833 hrs.			Res. Removed at 1698 hrs.			Res. Removed at 744 hrs.			Wicking a Problem		
GAS UTILIZATION/ SENSITIVITY	None						Not Air or H$_2$ Sensitive					
TOTAL HOURS	Life Test: 3257 H.C.D. Test: 2612			2106			2294			240		
REMARKS	Note Current Density			Temp. Overshoot Shutdown						Disassembled		

STACK NO.	354			355			356			357		
TEST OBJECTIVE	Double Matrix			High Current Density			High Current Density			Seamed Electrodes		
NO. CELLS	3			3			3			3		
ANODE mg Pt/cm^2	.55	.51	.58	.30	.25	.25	.26	.22	.29	.57	.57	.60
		Std			Std			Std			Std	
CATHODE mg Pt/cm^2	.92	.81	.88	.60	.56	.59	.57	.59	.62	.90	.92	.94
		Std			Std			Std			Std	
MATRIX	Double Kynol			SiC			SiC			Kynol		
PLATE/CONDITION	Good			Good			Fair			Good		
PEAK PERFORMANCE, Air-OCV- volts	.58 / .84	.58 / .82	.56 / .78	.61 / .75	.57 / .69	.56 / .71	.62 / .78	.63 / .72	.61 / .76	.60 / .84	.57 / .74	.63 / .88
PRESENT PERFORMANCE, Air-OCV- volts										.62 / .86	.46 / .70	.64 / .90
O$_2$ GAIN, volts	.07	.08	.08	.07	.08	.09	.05	.06	.07	.02	.34	.01
MΩ READING	5.6			4.2			4.2			5.0		
ACID HISTORY										3cc 1418 hrs.		
GAS UTILIZATION/ SENSITIVITY										Air Sensitive		
TOTAL HOURS	1045			408			2068			1969		
REMARKS	Disassembled			Disassembled			Disassembled					

TABLE III.4   STACK TESTING SUMMARY

Page 4 of 8

- Short Stacks (350 cm^2)
- 108 ASF (40 A)

STACK NO.	358			359			360			361		
TEST OBJECTIVE	5% Platinum			5% Platinum			Compression Studies			Compression & Acid Wicking		
NO. CELLS	3			3			3			3		
ANODE mg Pt/cm^2	.23 Pt 5/c	.34	.30 40 RC	.31 Pt 5/c	.29	.32 40 RC	Std			.28	.26 Std	.23
CATHODE mg Pt/cm^2	.51 Pt 5/c	.53	.53 40 RC	.5 Pt 5/c	-	.6 40 RC	Std			.56	.57 Std	.49
MATRIX	Kynol			SiC			Kynol			Kynol		
PLATE/CONDITION	Fair			Good			Good			Good		
PEAK PERFORMANCE, Air-OCV- volts	.61 .81	.61 .81	.61 .81	.58 .75	.64 .84	.51 .62	.47 .70	.52 .70	.53 .76	.56 .81	.58 .84	.53 .76
PRESENT PERFORMANCE, Air-OCV- volts												
O$_2$ GAIN, volts	.07	.07	.07									
MΩ READING	4.0											
ACID HISTORY												
GAS UTILIZATION/ SENSITIVITY				Air Sensitive			N/A			N/A		
TOTAL HOURS	1404			96			17			23		
REMARKS	Disassembled			Disassembled			Disassembled			Disassembled		

3/79

ENERGY RESEARCH CORPORATION

DEN3-67

STACK NO.	362			363			364			365		
TEST OBJECTIVE	Dry Room Wicking			TFE in Electrodes			Manifold Sealing			Backing Wetting		
NO. CELLS	3			3			3			3		
ANODE mg Pt/cm^2	.53	.62	.61	.54	.66	.63	.45	.42	.44	.44	.43	.44
		Std		Pt 10/c		45 RC		Std			Std	
CATHODE mg Pt/cm^2	.90	.99	.85	.64	.59	.60	.63	.57	.56	.58	.59	.58
		Std		Pt 10/C		45 RC		Std			Std	
MATRIX	Kynol			Kynol			Kynol			Kynol		
PLATE/CONDITION	Fair			Good			Good			Good		
PEAK PERFORMANCE, Air-CCV- volts	.56 .79	.59 .80	.59 .78	.56 .82	.57 .82	.54 .77	.52 .80	.54 .82	.52 .79	.59 .84	.58 .83	.57 .82
PRESENT PERFORMANCE, Air-OCV- volts				.56 .82	.56 .82	.52 .76						
O$_2$ GAIN, volts				.07	.07	.09						
MΩ READING	5.8			6.2								
ACID HISTORY				Res. Removed 609 Hrs.								
GAS UTILIZATION/ SENSITIVITY							N/A			N/A		
TOTAL HOURS	947			1232			20			16		
REMARKS	Disassembled			Horizontal			Disassembled			Disassembled		

TABLE III.4   STACK TESTING SUMMARY

- Short Stacks (350 cm^2)
- 108 ASF (40 A)

STACK NO.	366			367			368			369		
TEST OBJECTIVE	TFE in Electrode			45% TFE Cathode			Long Term Humidification No End Plate Seals			SRF Endurance		
NO. CELLS	3			3			3			3		
ANODE mg Pt/cm^2	.26	.26 Std	.24	.31	.19 Std	.30	.55	.56 Std	.59	.30	.28 Std	.30
CATHODE mg Pt/cm^2	.58 Pt 10/C	.58	.62 50 RC	.56 Pt 10/C	.48	.52 45 RC	.95	.94 Std	.91	.60	.59 Std	.59
MATRIX	Kynol			Kynol			Kynol			Kynol		
PLATE/CONDITION	Good			Good			Good			Good		
PEAK PERFORMANCE, volts Air- OCV-	.59 .82	.60 .83	.56 .81	.59 .83	.60 .83	.60 .83	.57 .83	.60 .84	.58 .84	.59 .83	.59 .85	.58 .85
PRESENT PERFORMANCE, volts Air- OCV-	.58 .82	.59 34	.56 .82	.56 .82	.57 .82	.57 .82	.57 .84	.60 .84	.57 .84	.57 .82	.58 .84	.57 .84
O$_2$ GAIN, volts	.08	.08	.07	.08	.07	.07	.07	.09	.07	.07	.09	.08
MΩ READING	5.4			5.4			5.6			4.6		
ACID HISTORY	Res. Removed at 609 Hrs.			Res. Removed at 615 Hrs.			Res. Removed at 258 Hrs.			Res. Removed at 238 Hrs.		
GAS UTILIZATION/ SENSITIVITY	2.5 Stoich Air 1.25 Stoich H$_2$			2.5 Stoich Air 1.25 Stoich H$_2$			None			Start SRF @ 243 Hrs.		
TOTAL HOURS	1151			1167			Life: 594 Humid.: 115			Life: 334 SRF: 89		
REMARKS	Horizontal			Horizontal			Horizontal					

TABLE III.4 STACK TESTING SUMMARY

- Short Stacks (350 cm^2)
- 108 ASF (40 A)

STACK NO.	370			371			372			373		
TEST OBJECTIVE	C Plate Extended Matrix			Backing Paper TFE			Acid Leak			Acid Leak		
NO. CELLS	3			3			3			3		
ANODE mg Pt/cm^2	.60	.58 Std	.59	.50	.55 Std	.60	.55	.60 Std	.66	.69	.54 Std	.60
CATHODE mg Pt/cm^2	.68	.58 Std	.60	.55	.58 Std	.55	.52	.70 Std	.68	.53	.66 Std	.55
MATRIX	Kynol			Kynol			Kynol			Kynol		
PLATE/CONDITION	Good			Good			Good			Good		
PEAK PERFORMANCE, Air- OCV- volts	.55 .85	.59 .86	.60 .84	.61 .87	.60 .86	.60 .86	.59 .87	.61 .89	.61 .88	.58 .88	.60 .87	.60 .87
PRESENT PERFORMANCE, Air- OCV- volts												
O$_2$ GAIN, volts				.08	.08	.08	.09	.09	.09	.09	.08	.07
MΩ READING	5.6			3.9			4.4			4.25		
ACID HISTORY				Wet Assembly			Wet Assembly			Wet Assembly		
GAS UTILIZATION/ SENSITIVITY				None			None			None		
TOTAL HOURS	174			66			87			44		
REMARKS	Disassembled			Disassembled			Disassembled			Disassembled		

ENERGY RESEARCH CORPORATION

3/79

Page No. 33

DEN3-67

STACK NO.	401	402	403	404	405
TEST OBJECTIVE	Scale-Up Dry Electrodes	Wet Electrodes	Electrode Prefilling	Electrodes & Matrices Prefilled	Endurance Thermal Analysis
NO. CELLS	5	5	5	5	5
ANODE mg Pt/cm^2	.58 (Avg) Std	.53 (Avg) Std	.50 (Avg) Std	.50 (Avg) Std	.60 (Avg) Std
CATHODE mg Pt/cm^2	.89 (Avg) Std	.90 (Avg) Std	.50 (Avg) Std	.50 (Avg) Std	.58 (Avg) Std
MATRIX	Kynol	Kynol	Kynol	Kynol	Kynol
PLATE/CONDITION	Good	Good	Good	Good	Good
PEAK Air- PERFORMANCE, OCV- volts	.60	.57	.55	.56	.58
PRESENT Air- PERFORMANCE, OCV- volts					.510
O$_2$ GAIN, volts	N/A	.083	.076		.078
MΩ READING	N/A	4.9	3.5		4.8
ACID HISTORY	Acid Supplied Regularly	Acid Supplied Regularly	Acid Need Was Observed	Acid Supplied Regularly	Acid Supplied Regularly
GAS UTILIZATION/ SENSITIVITY		None Noted	None Noted		Increasing Air Sensitivity
TOTAL HOURS	26	135	151	251	268
REMARKS	Disassembled	Disassembled	Disassembled	Shut Down	Still in Operation Horizontal

The following areas are being investigated:

1.   Backing paper wettability and acid leakage

2.   Acid volume change due to concentration

3.   External pressure applied to the stacks

1.   Backing Paper Wettability and Acid Leakage:

The backing paper is being treated with Teflon^R to make
it nonwettable. The extent of treatment has been controlled
for studying wettability of the paper. As indicated by Stacks
371, 372 and 373 in Table III.5, the Teflon content of the
backing paper does not seem to affect acid leakage. Since wet-
ting was observed at the seams (which could be reduced by care-
ful joining of the electrodes) the acid leakage is probably the
result of over-compression of the stack.

2.   Acid Volume Change Due to Concentration

It has been estimated that, if the acid concentration
changes from 100% to 96% by weight, the volume change is about
6% at 180°C. For our operation, the acid concentration in the
fuel cell is at approximately 98% for existing operating con-
ditions. Thus the acid concentration used in the prefilled
components has been changed from 102% to about 98% in the most
recent stacks. The effects of acid concentration in prefilled
components require further investigation.

3.   External Pressure Applied to the Stacks

Experiments have been designed to study the effect of
stack compression on acid leakage through the backing paper.
It has been observed in the previous stacks that the external
pressure applied between tie rods has some effect on performance.
Figure III.1 represents the ohmic resistance of Stack 376 as a

TABLE III.5

SUMMARY OF STACKS TESTED IN SUPPORT OF 1200 cm^2 STACKS

| STACK NO.	PURPOSE	VARIATIONS	OBSERVATIONS
371	Acid leak test – high Teflon content on backing paper	One piece rolled electrode, 46% Teflon	Performance decay started very early. Post-test analysis indicated acid leak through backing paper.
372	Acid leak test – medium Teflon content on backing paper	Seamed electrode, 36% Teflon	Leak through backing paper observed. Additional wetting at the seams.
373	Acid leak test – high Teflon content on backing paper	Seamed electrode, 46% Teflon	Acid leak observed similar to 371 & 372. More wetting at the seams.
374	Acid prefilling in components	99 wt% of acid was prefilled in electrodes & matrix.	Acid leak through backing. Backing paper observed compressed.
375	Acid prefilling thick shims	99 wt% of acid prefilled in components. Pressure up to 345 kPa (50 psia).	No acid leak through backing paper. No observable backing paper compression. Slightly higher resistance than the usual stacks.
376	Acid prefilling thick shims. Ohmic resistance variation as a function of compression.	98 wt% of acid prefilled in components.	No observation of acid leak through backing paper. See Figure III.1 for resistance data.

PRESSURE, psia

STACK 376,
RESISTANCE AT
OCV

OHMIC RESISTANCE OF STACK, mΩ

PRESSURE APPLIED ON STACK, kPa
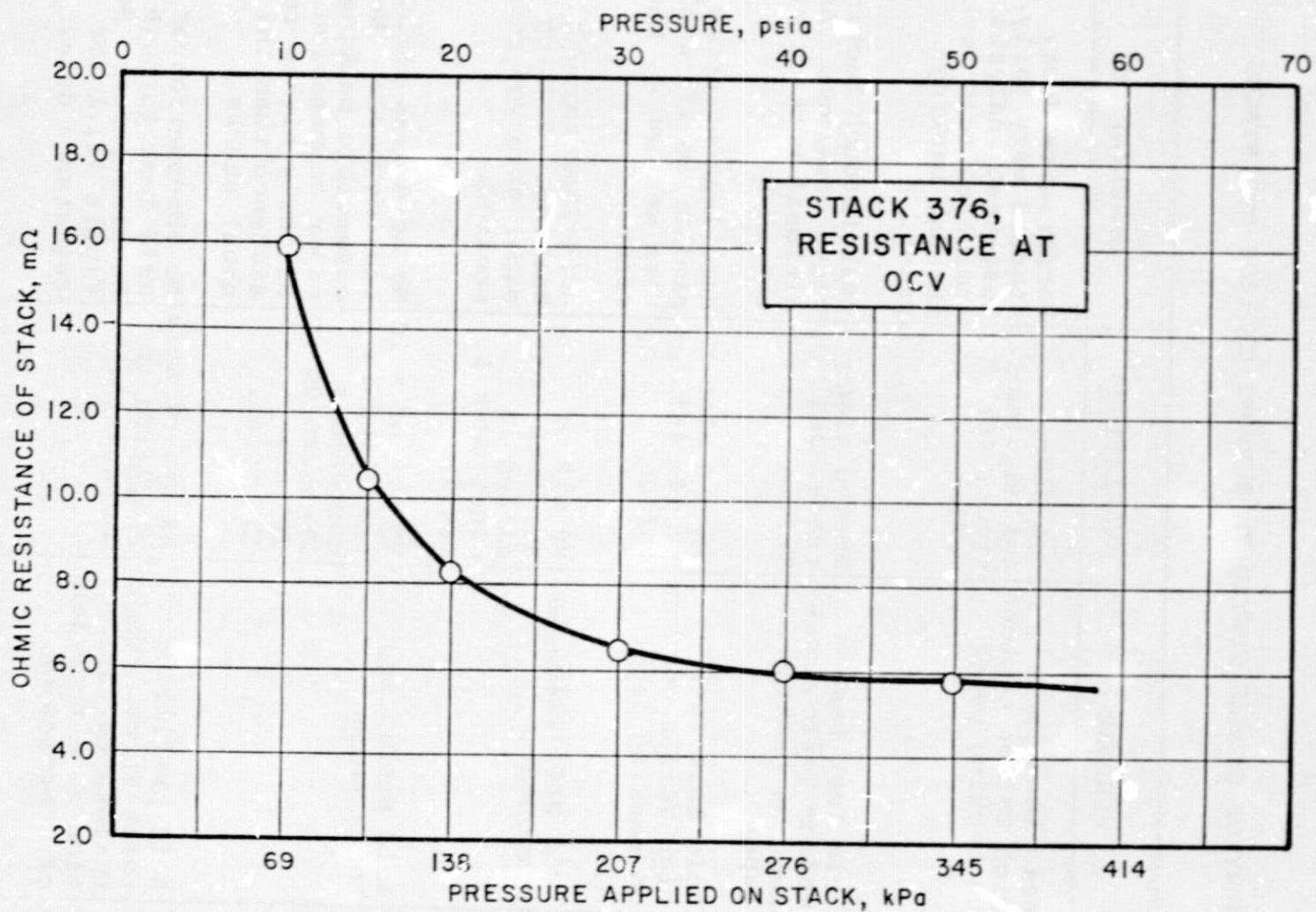
FIGURE III.1

OHMIC RESISTANCE OF THE STACK AS A FUNCTION
OF APPLIED PRESSURE

DEN3-67

function of pressure applied. Post-test analysis of this stack
revealed that much of the load was taken along the edges. Little
compression was observed for the matrices or the electrodes in
the center of the stack. The high resistance might be partly due
to poor contact between the backing paper and the bipolar plate
ribs.

B.   Effect of Operating Conditions

Operating conditions have been evaluated for the following
variables during this quarter:

1.   Dry gases vs humidified gases

2.   Current density

1.   Dry Gases vs Humidified Gases:

For the design of large stacks that operate by ambient air
and SRF, it is important to evaluate the effect of humidification.

Table III.6 represents the experiments conducted to evaluate
the effect of humidification at different temperatures. The inlet
oxidant was set at 5 stoich and the inlet hydrogen at 1.25 stoich
for all the data. An analysis of the results confirms that there
is only a small effect on humidifying the fuel and oxidant.

2.   Current Density

Higher current density tests are in progress. Performance
of Stack 349 has been steady at 0.57 terminal voltage for a cur-
rent density of 150 mA/cm^2.

C.   Component Evaluation in Stacks

Stacks which are assembled with dry components require a
few days of acid wicking. The wicking rate of acid depends on
the properties of the components and the dimensions of the stack.

TABLE III.6

DEW POINT TEMPERATURES OF INLET FUEL AND OXIDANT

Polarization Data Number	Dew Point Temperature of the Gas		
	Fuel	Oxidant	
	H_2	O_2	Air
1	27°C	27°C	---
2	27°C	----	Dry
3	32°C	----	Dry
4	38°C	----	Dry
5	-34°C	----	80
6	-34°C	----	90
7	-34°C	----	100
8	-34°C	----	Dry

Various possibilities of acid filling have been considered.
One such procedure involves assembly of stacks with prefilled
components. Stacks 374, 375 and 376 were assembled with cal-
culated amounts of acid. Preliminary results show that the
time required for prefilling of electrodes can be cut from
five days to one day. Experiments are being considered to
study performance, wettability of components and additional
acid supply mechanisms.

ENERGY RESEARCH CORPORATION

TASK IV.   SHORT STACK TESTING

4.1   Evaluation of the Stacks

A total of 4 short stacks have been tested in this quarter.
Table IV.1 summarizes the information obtained from these stacks
(402 through 405) along with Stack 401 started earlier. The
IR-free performance of selected cells equals the 350 cm^2 stacks.
Initial IR-free performance of Cell No. 1 in Stack 405 (1200 cm^2)
is compared with cells of 5 in. x 15 in. (350 cm^2) stacks (Fig-
ure IV.1). Performance of the 1200 cm^2 stacks decayed rather
rapidly because of crossleaks resulting from acid weeping through
the backing paper.

In order to improve performance, the temperature distribu-
tion of a cell should be maintained as uniform as possible.
Therefore, temperature profile readings were taken for each cell
in Stack 405. Figure IV.2 describes the temperature profile for
Cell No. 3 in this stack. Similar temperature profiles were ob-
tained for each cell.

TABLE IV.1

SHORT STACK TESTING

● Supportive Testing in 5" x 15" Stacks in Progress

| Stack No.	Average Acid Filling	Initial Avg. Perfor. Volts/Cell	Life in Hours	Average Life Performance	Remarks
401	Dry Electrodes	0.59	25	0.55	Gas Cross Leaks Stack Terminated
402	Very Wet Electrodes Wet Matrix	0.58	140	0.54	Gas Cross Leaks Backing Paper Wetness Stack Terminated
403	12 G. Acid in each Electrode Wet Matrix	0.57	100	0.50	Cross Leak Observed Stack Terminated
404	13 G. Acid in each Electrode Wet Matrix	0.55	170	0.54	Slight Cross Leak Repeated Acid Addition Stack in Operation
405	14 G. Acid in each Electrode Wet Matrix	0.57	70	0.55	Slight Cross Leak Stack in Operation
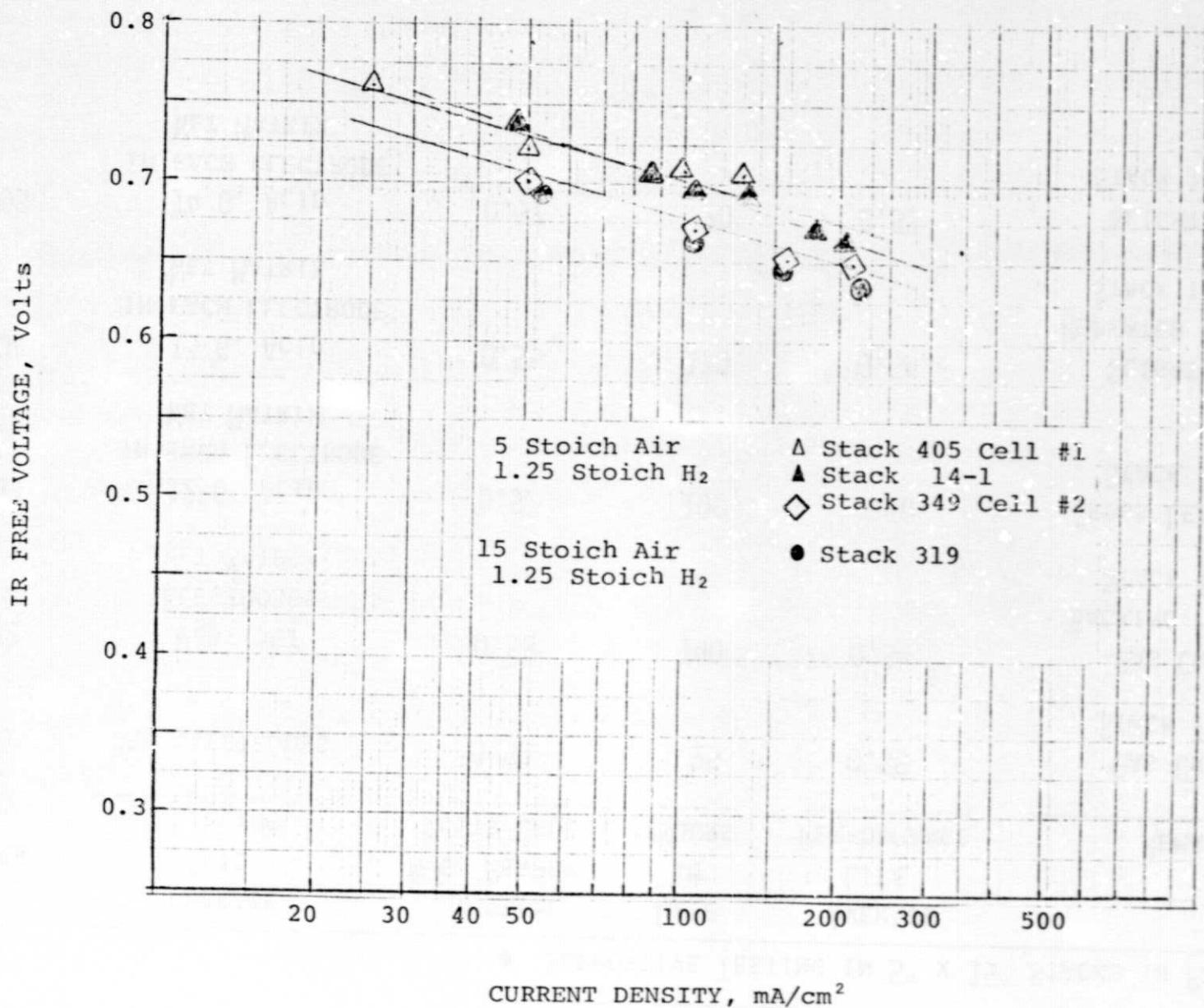
FIGURE IV.1   INITIAL PERFORMANCE OF CELL NO. 1 IN STACK 405

DEN3-67

D0485